Surfactant effects on doping of GaAs grown by organometallic vapor phase epitaxy

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Recently, the addition of the isoelectronic surfactant Sb during organometallic vapor phase epitaxy (OMVPE) of GaInP was shown to eliminate ordering, resulting in a significant change in the band gap energy. These results suggest that surfactants added during growth could have profound affects on other important properties of semiconductors, such as doping. This letter presents the results of a recent study on the effects of the isoelectronic surfactant Sb on doping in GaAs. The addition of a small amount of triethylantimony during OMVPE of GaAs is found, using secondary ion mass spectroscopy analysis, to increase the Zn doping concentration from $<6\times10^{18}$ atoms/cm^3 to 9×10^{18} atoms/cm^3, a factor of 1.6. The amount of antimony introduced into the solid is only $2-3\times10^{17}$ atoms/cm^3. The addition of Sb also increases the impurity concentration of In in GaAs, but does not affect the concentration of Te or P. © *2001 American Institute of Physics.*
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To control the properties of advanced semiconductor devices and structures, the surface properties must be controlled during vapor phase growth processes, in particular for organometallic vapor phase epitaxy (OMVPE) and molecular beam epitaxy. The use of surfactants to control the surface morphology, growth mode, and surface reconstruction during growth of elemental[1] and III/V[2–6] semiconductors has been demonstrated. Recently, the use of surfactants to change a major semiconductor property, the band gap energy, was reported.[7–9]

In vapor phase growth, surfactants typically refer to substances that accumulate at the surface during growth and alter the surface properties. Generally, surfactants are substances with a low solubility (i.e., they are rejected from the solid) and a low vapor pressure (i.e., they do not rapidly evaporate). This results in a high surface concentration of the surfactant that in turn can profoundly affect the surface energy, surface diffusion, surface reconstruction, adatom attachment, and step structure.[4]

This letter presents the results of a recent study on the effects of the isoelectronic surfactant Sb on doping in GaAs. Secondary ion mass spectroscopy (SIMS) depth profile measurements of doped GaAs samples grown by OMVPE with and without the addition of a small amount of triethylantimony (TESb) clearly indicate a change in the doping concentration. The addition of Sb increases the Zn doping concentration by a factor of 1.6. The addition of Sb also increases the impurity concentration of In in GaAs, but does not affect the concentration of Te or P.

All of the GaAs layers discussed in this letter were grown in a horizontal, infrared-heated, atmospheric pressure, OMVPE reactor. Semi-insulating GaAs substrates with singular (001) orientation were cleaned by standard degreasing followed by a 1 min etch in a 2 NH_4OH:12H_2O:1H_2O_2 solution. The substrates were then rinsed in de-ionized water for 5 min and blown dry with N_2 before being loaded into the reactor. Trimethylgallium (TMGa) at 7 °C and tertiarybutylarsine (TBA) at −7 °C were used as the organometallic precursors. TESb at −7 °C was used as the surfactant precursor. The TESb to group III ratio in the vapor was 0.012 for all of the doping experiments. Dimethylzinc with a Zn/III_V ratio of 0.08 and diethyltellerium with a Te/III_V ratio of 0.000 38 were used as dopants in the GaAs layers. The indium and phosphorus contamination seen in the GaAs layers is due to memory effects from the previous growth of GaInP. The carrier gas was Pd-diffused H_2. All of the layers were grown at a temperature of 620 °C with a V/III ratio of 40, a total flow rate of 5200 ml/min, a growth rate of 1.3 μm/h, and a TMGa partial pressure in the vapor of 2.0×10^{-2} Torr. During growth of the GaAs layers, the dopant was added during the entire 36 min deposition. TESb was added after 12 min of deposition and removed after 12 additional min of growth. All of the GaAs layers were smooth and mirror-like when examined using Nomarski phase contrast optical microscopy. SIMS depth profiles of the doped GaAs layers were performed by Applied Microanalysis Laboratory using a Cameca ims-3f system. A Cs^+ primary beam was used to analyze the GaAs layers for Sb^-, Te^-, and P^-, and an O_2^+ primary beam was used to analyze for Zn^+ and In^+.

Figure 1 shows the SIMS depth profile of a Zn doped GaAs epilayer. As expected, at a constant DMZn concentration in the vapor ($Zn/III_V=0.08$), the Zn concentration in the layer slowly builds up to concentration of 5.8×10^{18} atoms/cm^3. However, when a small amount of TESb is added to the vapor (Sb/III=0.012) the Zn concentration in the layer increases sharply to 8.5×10^{18} atoms/cm^3, a 60% increase. As can be seen, the Sb concentration in the layers is very small ($2-3\times10^{17}$ atoms/cm^3). Note that after the TESb is removed from the vapor, as indicated by a decrease in the Sb concentration in the epilayer, the Zn concentration decreases as well. The correlation between the change in the Zn and Sb concentrations in the layer clearly indicates that Sb affects the incorporation of Zn in GaAs.

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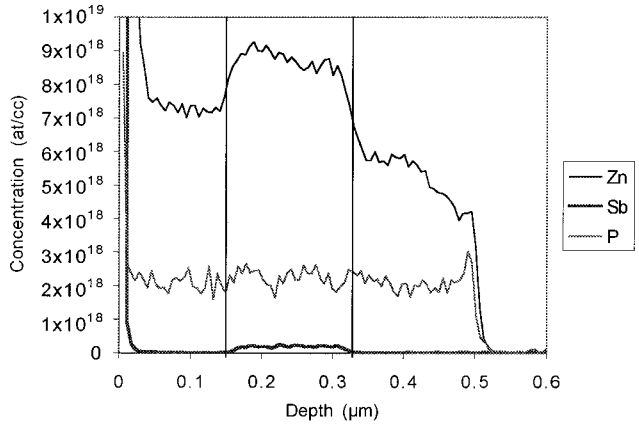

FIG. 1. SIMS depth profile of Zn doped GaAs epilayer grown with a Zn/III ratio in the vapor of 0.08. After 12 min of growth, a small amount of TESb ($Sb/III_V=0.012$) was added to the system. 12 min later, the Sb was removed and an additional 12 min of Zn doped GaAs was grown.

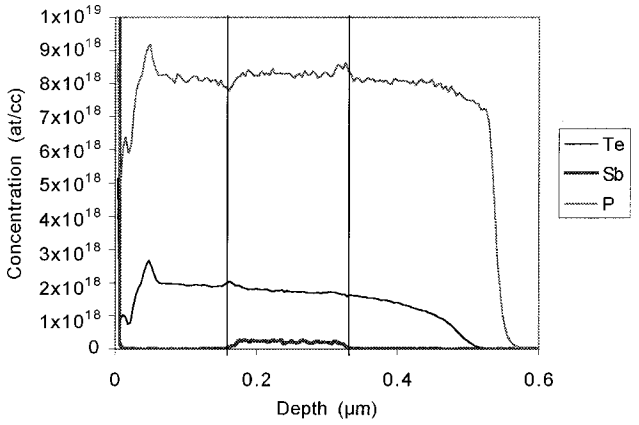

FIG. 3. SIMS depth profile of Te doped GaAs epilayer grown with a Te/III ratio in the vapor of 0.000 38 and a Sb/III ratio in of vapor of 0.012. The deposition cycle followed the same three step process described for Fig. 1.

It has been shown previously that Sb acts as a surfactant in GaInP. For example, surface photoabsorption measurements have shown that a small amount of TESb significantly changes the surface reconstruction of GaInP.[8] It is expected that Sb also acts as a surfactant in GaAs. Therefore, it is, perhaps, not surprising that a small amount of Sb can affect the incorporation of dopants in GaAs. The SIMS data shown in Fig. 1 are direct evidence that the surfactant Sb affects dopant incorporation.

The affect of the surfactant Sb on other dopants was also investigated. Figure 2 shows the SIMS depth profile of a GaAs epilayer that was inadvertently doped with In. The In contamination is due to memory effects from the previous growth of GaInP layers. The correlation between the change in the In and Sb concentrations strongly suggests that the surfactant Sb also affects the incorporation of In in GaAs.

Figure 3 shows the SIMS depth profile of a Te (donor) doped GaAs epilayer. The DETe was held constant at a Te/III_V ratio of 0.000 38. In this case, the addition of TESb ($Sb/III_V=0.012$) during growth did not change the Te concentration. The Sb concentration in the layer is similar to that in the Zn and In doping experiments which indicates that Sb did collect on the surface during growth of the Te doped GaAs. This suggests that the mechanism for Te incorporation is different than for Zn and In. Note that Zn and In both reside on group III sites; whereas, Te, an *n*-type dopant, is incorporated on group V sites.

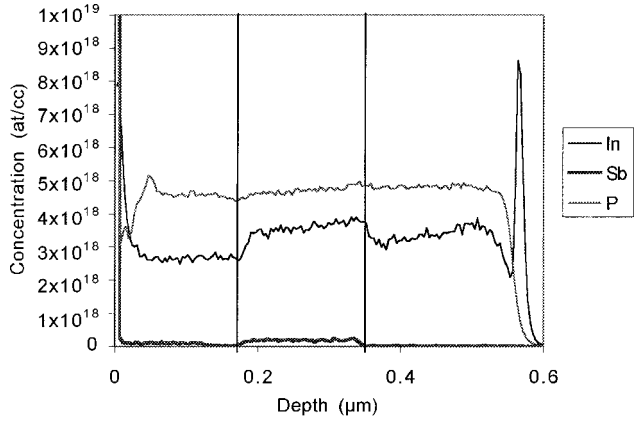

FIG. 2. SIMS depth profile of In doped GaAs epilayer. In (and P) contamination are from a system memory effect. An Sb/III ratio in the vapor of 0.012 was used. The deposition cycle followed the same three step process described for Fig. 1.

As shown in Figs. 1, 2, and 3, the concentration of P inadvertently present in the GaAs epilayers was also measured. Apparently, Sb has little affect on the concentration of P, which is incorporated on group V sites. As was the case for In, the P contamination most likely came from memory effects. The P concentration is the highest (8.2×10^{18} atoms/cm^3) in the Te doping experiment (Fig. 3) which was the first GaAs epilayer to be grown after the growth of GaInP. The P concentration decreased which each consecutive GaAs deposition. The lowest P concentration (2.0×10^{18} atoms/cm^3) was seen in the last GaAs deposition, shown in Fig. 1.

The effect of the surfactant Sb on the In distribution coefficient is the most easily analyzed. Clearly, at the growth temperature used in these experiments, 620 °C, some of the In reaching the surface is able to evaporate before being incorporated; otherwise, there could be no clear explanation for the increase of In incorporation due to Sb on the surface. This suggests that the Sb acts to inhibit In evaporation. However, this is not likely due to stronger bonding of In to the Sb-covered surface, since In–Sb bonds are known to be much weaker than In–As bonds. The classical theory of elemental incorporation into the solid[10] suggests that In evaporation occurs as it diffuses on the (001) terrace, before being incorporated into the crystal lattice by attachment at a step edge. In this case, the ability of In to be incorporated is related to the probability of In reaching a step edge and sticking there. Thus, either an increase in group III adatom surface diffusion coefficient or an increase in the group III sticking coefficient at the step edge would cause an increase in In incorporation into the GaAs. Studies of the effect of the surfactant Sb on lateral compositional modulation in GaInP suggests that Sb does, indeed, increase the surface diffusion coefficients of Ga and In on the (001) surface.[11] It is also possible that Sb will increase the sticking coefficient of group III adatoms at $[-110]$ step edges, due to occupation of the ''dangling'' group V sites at the step edge by Sb, since Sb has a much lower volatility than As.[12] In fact, Sb is observed to increase the step velocity somewhat.

This mechanism also explains the increase in Zn incorporation, since Zn also incorporates on the group III sublattice. In addition, the lack of a change in incorporation of elements occupying the group V sublattice, (i.e., Te and P) is explained, since neither effect described above changes group V incorporation into the solid.

This work indicates that an isoelectronic surfactant such as Sb can affect dopant incorporation in GaAs. The addition of small amounts of TESb during growth of GaAs epilayers by OMVPE significantly affects the incorporation of Zn and In, but not Te and P. The effect of surfactants on doping provides insights into the mechanism for atomic incorporation during vapor phase growth of semiconductors. This reconfirms the importance of surface processes during OMVPE. The ability to control major semiconductor properties, such as conductivity type and concentration, by simply adding a small amount of surfactant during OMVPE growth may profoundly affect the manufacturing of many important semiconductor devices.

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